

Factors Affecting the Analytical Response of Electroactive Polymers

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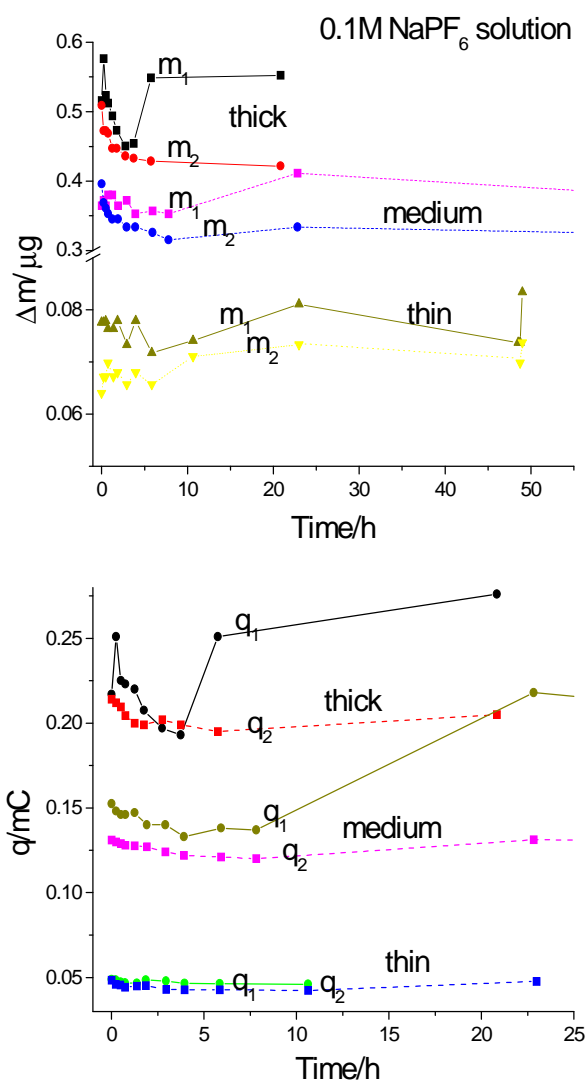
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A stable electrochemical response is a prerequisite for using an electroactive polymer as a component in a device. Meeting this requirement is not a simple task, considering the various processes that may occur in an electroactive polymer film. Here we consider a few of the processes that we believe are exhibited by a wide range of these polymers and which could reduce the reliability of a device based on them. We draw our examples from potentiodynamic EQCM experiments, specifically cyclic voltammetry starting with a reduced poly(vinylferrocene) film (PVF). Here we consider phenomena that occur on two experimental times scales, those on a single day, and those that occur over much longer times.

On a single day, we assume that the film has been held at constant potential until it is in pseudo equilibrium with its environment, i.e., its polymer configuration and solvent content are not changing at a significant rate on this short experimental time scale. After the first potential cycle, such a film almost always exhibits a decrease in mass and charge capacity. This mass decrease can be separated into a solvent and counter ion components, usually unequal in magnitude. These effects depend on the nature of the counter ion and the electroactive polymer. In the case of PVF it becomes more pronounced as the counterion changes from tetrafluoroborate to perchlorate to hexafluorophosphate to p-toluenesulfonate to naphthalenesulfonate. The magnitude of the trapping phenomena increases with the potential scan rate. Also, the oxidation cycle of the cyclic voltammogram exhibits two partially resolved peaks whose heights and potentials change between the first two potential scans. This suggests that different species exist during the second potential scan than those that existed initially (at pseudo equilibrium).

As a film ages from the time of preparation other phenomena occur. Mass and charge trapping, are always seen, as is the difference in the oxidation portion of the cyclic voltammogram between the first and subsequent cycles. Ageing results obtained with sodium hexafluorophosphate are shown in Figure 1. The most significant effect with PVF is an initial decrease of the charge and mass change in the first three hours of film ageing for a film that has been held at open circuit in a bathing electrolyte. There is no clear pattern for the behavior seen with the different anions we studied if the charge and mass changes are normalized with respect to a new film. This counter ion dependence suggests that the transfer of neutral species (solvent) may be important.

Continuous cycling causes a substantial decrease of the amount of available charge and mass change. Also, if an aging film is open circuited for few days, (a) and the charge and mass change measured over a potential cycle, and then (b) held at 0 V before being potential cycled



again, the available charge and mass change increases, but not to the level obtained with a freshly prepared film.

We propose an explanation for these phenomena based on a time dependent change in polymer configuration using a model that takes into account counter ion and solvent trapping for these various polymer forms.

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Figure 1. Effect of aging on the total mass and charge changes accompanying the redox switching of a PVF film in 0.1 M sodium hexafluorophosphate solution. Subscripts indicate either the first or second potential cycle. Voltage scan rate = 0.050 V s⁻¹.